

# PATENT SPECIFICATION

(11) 1345 653

1345 653

- (21) Application No. 25893/72 (22) Filed 2 June 1972  
 (31) Convention Application No. 7120051 (32) Filed 3 June 1971 in  
 (33) France (FR)  
 (44) Complete Specification published 30 Jan. 1974  
 (51) International Classification B01J 11/78 C07C 17/02  
 (52) Index at acceptance

BIE 200 20Y 330 33Y 341 34Y 491 49Y 510 515 521  
 691 693  
 C2C 20Y 304 313 31Y 339 410 412 413 414 418 440  
 44Y 562 567 65Y 73Y HA

(72) Inventor JEAN-CLAUDE DAUMAS

## (54) CATALYSTS FOR THE OXYCHLORINATION OF ETHYLENIC HYDROCARBONS IN A FLUID OR MOVING BED



(71) We, RHONE-PROGIL, a body corporate organised and existing under the laws of France, of 6 rue Piccini, 75-Paris 16e, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a catalyst for the oxychlorination of ethylenic hydrocarbons, especially of ethylene in a fluid or moving bed.

The importance of oxychlorinating ethylenic hydrocarbons and more especially ethylene in the production of various chlorinated derivatives is known, the most important of the chlorinated derivatives being 1,2 - dichloroethane which is used as a source of vinyl chloride upon which the manufacture of many plastics materials is based.

It is known that catalysts for use in the oxychlorination of hydrocarbons may be derived from well-known Deacon catalysts intended to promote the reaction of gaseous hydrogen chloride on gases containing molecular oxygen to produce chlorine. Catalysts of the Deacon type having many different formulae have been recommended. Copper is frequently the principle active element of these catalysts and is almost always in the form of a chloride. Such catalysts also include various additives intended to increase their heat-stability and activity. The additives vary very widely and include a large number of metals such as alkali metals, alkaline-earth metals, magnesium, beryllium, chromium, cobalt, nickel, manganese, vanadium, tin, iron, bismuth, antimony, uranium, scandium and various rare earth metals. The active elements are disposed on carriers which are no less varied. The carriers usually comprise oxides, in particular aluminium, silicon and magnesium oxides, which oxides frequently occur in the state of natural combinations or

associations, such as pumice stone, clays and bauxites.

These different catalysts make it possible to produce a large number of chlorinated hydrocarbons by reaction of various hydrocarbons, as chlorine acceptors, with a gaseous mixture containing hydrogen chloride and oxygen. However, not only the proportions of starting materials and the reaction conditions, but also the nature of the catalyst must be chosen according to the desired results and the hydrocarbon to be chlorinated. Moreover, the catalyst used should enable degradation of the hydrocarbons by oxidation, and the conversion thereof into heavy complex halogenated substances which are difficult to use, to be avoided so far as possible.

In the oxychlorination of ethylenic hydrocarbons, particularly of ethylene to 1,2 - dichloroethane, it is known that, in order to obtain the best yields, it is advantageous to operate at low temperatures, which in practice must be lower than 300°C and preferably lower than 250°C. Therefore attempts have been made to precisely define catalysts that are sufficiently active at these temperatures.

For this latter purpose, catalysts have been recommended which, in addition to copper, comprise rare-earth metals and alkali metals, the latter being included for the purpose of reducing the volatility of the copper. In these catalysts the catalytic elements are supported on any carrier, especially active porous silica.

However, it has recently been found that the results obtainable using this general class of catalysts can be greatly improved. In our copending patent Application Number 48346/70, Serial No. 1326428, it is shown that the yield of 1,2 - dichloroethane obtainable by the selective oxychlorination of ethylene can be increased by using a catalyst that comprises copper and some of the rare-earth metals on a carrier comprising alumina having a surface area sufficient to be active at the low temperatures which cannot be exceeded

[Price 25p]

without reducing the selectivity, and is devoid of alkali metal compounds, which have a tendency to reduce the activity of the catalyst without improving the stability of the copper in the catalyst.

It has now been found that catalysts that comprise copper and magnesium, preferably in the form of their chlorides, on a carrier comprising alumina which is sufficiently active to allow oxychlorination to occur at the low temperatures which must be observed to safeguard selectivity, and are devoid of alkali compounds enable combustion occurring during the selective oxychlorination of ethylenic hydrocarbons carried out industrially at low temperatures to be reduced and the desired product to be obtained in a good yield and with good selectivity. According to the invention there is provided a catalyst for the selective oxychlorination of ethylenic hydrocarbons in a fluid or moving bed, said catalyst consisting of copper and magnesium in the form of their chlorides or other compounds convertible to the chlorides during the oxychlorination, and active alumina having a surface area of from 180 to 380 sq.m/g, the percentage by weight of copper in the catalyst being from 3 to 10, this percentage corresponding to the case where the copper and magnesium are present in the form of, or have been converted to, cupric chloride and magnesium chloride, and the ratio Mg/Cu, expressed in atoms, being from 0.2 to 0.8.

Catalysts in accordance with the invention are sufficiently active to permit oxychlorination to be effected at temperatures below 250°C.

The invention also provides a process for selectively oxychlorinating ethylenic hydrocarbons, especially ethylene, which is carried out at a temperature below 300°C or even below 250°C, in the presence of a catalyst of the invention. Using this process it is possible to obtain high yields of chlorinated hydrocarbons, e.g. 1,2 - dichloroethane, with little occurrence of combustion.

The actual surface area of the active alumina and the actual amounts of copper and magnesium present in any particular catalyst should be determined conjointly according to the general conditions under which the catalyst is to be used.

Although the catalysts according to the invention can be prepared by various methods, they are preferably prepared by impregnating the active alumina, one or more times, with one or more solutions providing the compounds of copper and magnesium. The copper and magnesium compounds may be provided by separate solutions or by solutions containing both these compounds.

In the following Examples, results obtained when ethylene was oxychlorinated on a laboratory scale and in pilot operations in the presence of various catalysts according to the

invention and in the presence of some other catalysts are compared. Due to the large number of parameters involved, no examples are given in which the results obtained for various compositions of the reaction gases and for various flow-rate and pressure conditions are compared. However the temperature, variations in which result in considerable changes in the results attained, is varied in some cases. All the laboratory tests are carried out in a fluid bed in a reaction vessel with a diameter of 20 mm, containing 25 cc of catalyst, and supplied at atmospheric pressure with a gaseous mixture of air, hydrogen chloride and ethylene in which the ratio HCl/C<sub>2</sub>H<sub>4</sub> is 2.25 and the ratio O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> is 0.7, the rate of flow of the gaseous mixture being 10 cm/s and the contact time being 1 s; the results obtained in the laboratory tests are verified in a pilot operation in a reaction vessel with a diameter of 600 mm, operating at atmospheric pressure, the ratio HCl/C<sub>2</sub>H<sub>4</sub> being equal to 2, the ratio O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> being 0.62, and the contact time being about 10 s.

#### EXAMPLE 1

In this Example the results obtained using catalysts containing varying amounts of copper and a constant amount of magnesium with respect to the copper, the Mg/Cu atomic ratio being fixed at 0.4, are compared. In each of the catalysts the carrier is active alumina in the form of microballs having diameters of from 20 to 125 μm and a surface area of 365 sq.m/g. The catalysts are prepared by impregnating the carrier with solutions containing cupric chloride and magnesium chloride in the amounts and concentrations required to produce the required concentrations of active elements in the catalysts obtained after drying the impregnated carrier.

The various catalysts are used in the oxychlorination of ethylene at 235°C, in accordance with the above specified conditions.

Characteristics of the catalysts and the results obtained are given in Table 1 below, in which X<sub>G</sub> expresses the overall conversion of ethylene and X<sub>CO<sub>2</sub></sub> expresses the combustion of ethylene.

TABLE 1  
%by weight of Cu in  
the catalysts (Mg/Cu  
ratio=0.4) Carrier-  
active alumina 365  
sq.m/g

	X <sub>G</sub>	X <sub>CO<sub>2</sub></sub>	
2.5	35	0.02	
3	45	0.05	
4.3	52	0.10	
5	58	0.15	
6	65	0.2	125
6.9	73	0.2	
9.5	75	0.25	
11	76	0.35	

These results clearly show that when the weight of copper in the catalyst is below 3%,  $X_G$  is too low, i.e. the catalyst has insufficient activity, and that increasing the amount of copper in the catalyst above 10% is useless since there is virtually no longer any increase in  $X_G$  and combustion begins to increase more rapidly when the proportion of copper exceeds this value.

#### EXAMPLE 2

In this Example the results obtained using

catalysts in which the ratio Mg/Cu is varied are compared. The % by weight of copper is fixed at 7 and the catalysts are prepared in the general manner described in Example 1 using a carrier identical to that used in Example 1. The catalyst are used in the oxychlorination of ethylene at 220°C and 235°C, in accordance with the above specified conditions.

Characteristics of the catalysts and the results obtained are given in Table 2 below.

TABLE 2

Ratio Mg/Cu in the catalysts (% by weight of Cu=7) Active alumina carrier—365 sq.m/g

Temperature °C	X <sub>G</sub>	X <sub>CO<sub>2</sub></sub>
235	70	0.6
220	57	0.2
235	73.2	0.4
220	59	0.1
235	73	0.1
220	58.5	0.02
235	72	0.3
220	51	0.03
235	64	0.45
220	45	0.05

These results clearly show the usefulness of the magnesium, but also show that the presence of an excessively large proportion of manganese with respect to the copper results in a reduction in the activity of the catalyst and an increase in the combustion, the acceptable range for the ratio Mg/Cu being from 0.2 to 0.8.

#### EXAMPLE 3

In this Example the results obtained using

catalysts containing identical amounts of copper and magnesium but whose active alumina carriers have different surface areas are compared. Each of the catalysts is prepared in the general manner described in Example 1.

Characteristics of the catalysts and the results obtained when the catalysts are used in the oxychlorination of ethylene at a temperature of 235°C are given in Table 3 below.

TABLE 3

Surface area of the catalyst carrier in Sq.m/g (% by weight of copper: 5.6; Mg/Cu ratio=0.37)

$X_G$	$X_{CO_2}$
16	0
47.5	0.1
55	0.15
61	0.2
63	0.30

These results clearly show that when the surface area of the carrier falls below 180 sq.m/g, the activity of the catalyst becomes too low and that when the surface area of the catalyst reaches about 380 sq.m/g combustion has a tendency to increase excessively, with-

out any compensating gain in the activity of the catalyst.

#### EXAMPLE 4

In this Example the results obtained using two catalysts according to the present invention, and a reference catalyst containing only

copper in pilot tests carried out in the manner specified above, operation being under optimum industrial conditions, are compared. Each of the catalysts is prepared by impregna-

tion of the carrier with (a) solution(s) of the metal chloride(s).

Characteristics of the catalysts, and the results obtained are given in Table 4 below.

TABLE 4

	Catalysts	Temperature °C	X <sub>G</sub>	X <sub>CO</sub>
10	Active alumina 350 sq.m/g 7% by weight Cu. Atomic ratio Mg/Cu =0.35	220	99.8	5
15	Active alumina 180 sq.m/g 6% by weight Cu. Atomic ratio Mg/Cu =0.35	230	99	2.5
	Active alumina 350 sq.m/g 10% by weight Cu	230	99.5	6

These results show that less combustion occurs when the catalysts containing magnesium are used. It should be noted that, in these pilot tests in which the contact time is approximately ten times longer than in the laboratory tests, the combustion and proportion of reacted ethylene are necessarily much higher. It should be noted also that comparable results are obtained using the two catalysts containing magnesium only because the temperature at which the catalyst produced on active alumina having a surface area of 180 sq.m/g is used is 10°C higher than that at which the catalyst produced on active alumina having a surface area of 350 sq.m/g is used. This clearly shows that the alumina used as the carrier must be sufficiently active.

#### WHAT WE CLAIM IS:—

1. A catalyst for the selective oxychlorination of ethylenic hydrocarbons in a fluid or moving bed, said catalyst consisting of copper and magnesium in the form of their chlorides or other compounds convertible to the chlorides during the oxychlorination, and active alumina having a surface area of from 180 to 380 sq.m/g, the percentage by weight of copper in the catalyst being from 3 to 10, this percentage corresponding to the case where the copper and magnesium are present in the form of, or have been converted to,

cupric chloride and magnesium chloride, and the ratio Mg/Cu, expressed in atoms, being from 0.2 to 0.8.

2. A catalyst according to claim 1, prepared by impregnating the active alumina with one or more solutions providing the compounds of copper and magnesium.

3. A catalyst according to claim 1, substantially as hereinbefore described in any one of the Examples.

4. A process for selectively oxychlorinating an ethylenic hydrocarbon carried out at a temperature of below 300°C in the presence of a catalyst according to claim 1 or 2.

5. A process according to claim 4, in which the ethylenic hydrocarbon is ethylene.

6. A process according to claim 4 or 5, in which the temperature is below 250°C.

7. A process according to claim 4, substantially as hereinbefore described in any one of the Examples.

8. Chlorinated hydrocarbons when prepared by a process according to claim 4, 5, 6 or 7.

For the Applicants,  
D. YOUNG & CO.,  
Chartered Patent Agents,  
9/10 Staple Inn,  
London, W.C.1.